

What is claimed is:

1. A hot-dip galvanized steel sheet comprising:
a plating layer consisting essentially of a η phase; and
an oxide layer disposed on a surface of the plating layer,
said oxide layer having an average thickness of 10 nm or more;
and
the oxide layer comprising a Zn-based oxide layer and an Al-based oxide layer, the Zn-based oxide layer having a Zn/Al atomic concentration ratio of more than 1 and the Al-based oxide layer having a Zn/Al atomic concentration ratio of less than 1.
2. The hot-dip galvanized steel sheet according to claim 1,
wherein
the plating layer has concavities and convexities on the surface thereof ; and
the Zn-based oxide layer is disposed at least on the concavities.
3. The hot-dip galvanized steel sheet according to claim 1,
wherein
the Zn-based oxide layer has microirregularities; and
the microirregularities have a mean spacing (S) determined based on a roughness curve of 1,000 nm or less and an average roughness (Ra) of 100 nm or less.

4. The hot-dip galvanized steel sheet according to claim 1, wherein

the Zn-based oxide layer comprises an oxide containing Zn and Fe; and

the Zn-based oxide layer has a Fe atomic concentration ratio of 1 to 50 atomic percent, the atomic concentration ratio being defined by an expression $\text{Fe}/(\text{Zn} + \text{Fe})$.

5. The hot-dip galvanized steel sheet according to claim 1, wherein the Zn-based oxide layer has an areal rate of 15% or more with respect to the surface of the plating layer.

6. The hot-dip galvanized steel sheet according to claim 1, wherein the oxide layer has an average thickness of 10 to 200 nm.

7. The hot-dip galvanized steel sheet according to claim 1, wherein the Zn-based oxide layer has microirregularities with a network structure including convexities and discontinuous concavities surrounded by the convexities.

8. The hot-dip galvanized steel sheet according to claim 1, wherein the Zn-based oxide layer has a Zn/Al atomic concentration ratio of 4 or more.

9. The hot-dip galvanized steel sheet according to claim 8, wherein the Zn-based oxide layer has an areal rate of 70% or more with respect to the surface of the plating layer.

10. The hot-dip galvanized steel sheet according to claim 8, wherein the Zn-based oxide layer is disposed on the concavities of the surface of the plating layer formed by temper rolling, and on the convexities or planar portions other than the concavities.

11. The hot-dip galvanized steel sheet according to claim 8, wherein

the Zn-based oxide layer comprises an oxide containing Zn and Fe; and

the Zn-based oxide layer has a Fe atomic concentration ratio defined by an expression $\text{Fe}/(\text{Zn} + \text{Fe})$ being 1 to 50 atomic percent.

12. The hot-dip galvanized steel sheet according to claim 8, wherein

the Zn-based oxide layer has microirregularities; and

the Zn-based oxide layer has a network structure that is formed by convexities and discontinuous concavities surrounded by the convexities.

13. A hot-dip galvanized steel sheet, comprising

a plating layer consisting essentially of a η phase; and

a Zn-based oxide layer containing Fe disposed on the surface of the plating layer,

the Zn-based oxide layer having an Fe atomic concentration ratio of 1 to 50 atomic percent, the Fe atomic concentration ratio being defined by the expression $\text{Fe}/(\text{Fe} + \text{Zn})$.

14. The hot-dip galvanized steel sheet according to claim 13, wherein the Zn-based oxide layer has microirregularities with a network structure including convexities and discontinuous concavities surrounded by the convexities.

15. The hot-dip galvanized steel sheet according to claim 13, wherein the Zn-based oxide layer has an areal rate of 15% or more with respect to the surface of the plating layer.

16. A hot-dip galvanized steel sheet, comprising
a plating layer consisting essentially of a η phase; and
a Zn-based oxide layer containing Fe disposed on a surface of the plating layer,

the Zn-based oxide layer having microirregularities with a network structure including convexities and discontinuous concavities surrounded by the convexities.

17. The hot-dip galvanized steel sheet according to claim 16, wherein the Zn-based oxide layer has a mean spacing (S) determined

based on a roughness curve being 10 to 1,000 nm and an average roughness (Ra) of 4 to 100 nm.

18. The hot-dip galvanized steel sheet according to claim 16, wherein the Zn-based oxide layer has an areal rate of 70% or more with respect to the surface of the plating layer.

19. The hot-dip galvanized steel sheet according to claim 16, wherein the Zn-based oxide layer is disposed on the planar portions of the surface of the plating layer other than the concavities formed by temper rolling.

20. The hot-dip galvanized steel sheet according to claim 19, wherein, the Zn-based oxide layer, which is disposed on the planar portions, has a mean spacing (S) determined based on the roughness curve of 10 to 500 nm and the average roughness (Ra) of 4 to 100 nm.

21. A method for producing a hot-dip galvanized steel sheet, comprising the steps of:

hot-dip-galvanizing a steel sheet to form a hot-dip galvanized layer;

temper-rolling the steel sheet provided with the hot-dip galvanized layer; and

subjecting the temper-rolled steel sheet to an oxidation treatment by bringing the temper-rolled steel sheet into contact

with an acidic solution having a pH buffering effect, and retaining the temper-rolled steel sheet in the solution for 1 to 30 seconds before washing with water.

22. The method according to claim 21, further comprising an activation step of activating the surface before or after the temper rolling step.

23. The method according to claim 22, wherein the activation step further comprises controlling an Al-based oxide content in a surface oxide layer before the oxidation step so that an Al concentration is less than 20 atomic percent.

24. The method according to claim 22, wherein the activation step comprises bringing the steel sheet into contact with an alkaline solution with a pH of 11 or more at 50°C or more for 1 second or more.

25. The method according to claim 22, wherein the activation step is performed before the temper rolling step.

26. The method according to claim 21, wherein the acidic solution contains 1 to 200 g/l of Fe ions.

27. A method for producing a hot-dip galvanized steel sheet,

comprising the steps of:

hot-dip-galvanizing a steel sheet to form a hot-dip galvanized layer;

temper-rolling the steel sheet provided with the hot-dip galvanized layer;

subjecting the temper-rolled steel sheet to an oxidation treatment by bringing the temper-rolled steel sheet into contact with an acidic solution having a pH buffering effect and containing 5 to 200 g/l of Fe ions with a pH of 1 to 3, and retaining the temper-rolled steel sheet in the solution for 1 to 30 seconds before washing with water; and

activating the surface before or after the temper rolling step.

28. A method for producing a hot-dip galvanized steel sheet, comprising the steps of:

hot-dip-galvanizing a steel sheet to form a hot-dip galvanized layer;

temper-rolling the steel sheet provided with the hot-dip galvanized layer;

subjecting the temper-rolled steel sheet to an oxidation treatment by bringing the temper-rolled steel sheet into contact with an acidic solution having a pH buffering effect with a pH of 1 to 5, and retaining the temper-rolled steel sheet in the solution for 1 to 30 seconds before washing with water; and

activating the surface before or after the temper rolling step.